CORRECTIONS APPLIED TO THE LDEO UNDERWAY pCO_2 MEASUREMENTS MADE ABOARD THE R/V *GOULD*, R/V *PALMER* AND USCGC *HEALY*

Taro Takahashi and Stewart C. Sutherland
Lamont-Doherty Earth Observatory of Columbia University

(August 25, 2015)

ABSTRACT

Since 1994, approximately 2.3 million pCO_2 measurements have been made in the surface waters of the polar oceans aboard three ships, aboard RVIB *Palmer*, RV *Gould* and USCGC *Healy* using an underway method developed and operated by the Lamont-Doherty Earth Observatory (LDEO) group. These data were reported to the CDIAC in a series of annual reports after the preliminary quality control. A recent reanalysis of the data has shown that these reported data call for minor corrections that account for the transit time of pumped sample water from the intake port near the bow to the pCO_2 system located some distance away. The methods used and the corrections applied are described in this report. The corrections applied to each data point are up to about ±8 uatm for the Palmer and Gould data and ±16 uatm for the Healy data, while the mean of the corrections for each cruise is less than ± 1 uatm. 2.3 million pCO_2 data reported from these three ships have been corrected for the time lag in Version 2014 of the LDEO Surface pCO_2 database as described in this report.

Please, site this report as:

Takahashi, T. and S.C. Sutherland, S. 2015. Corrections applied to the LDEO underway pCO_2 measurements made aboard the R/V *Could*, R/V *Palmer* and USCGC *Healy*. CDIAC Report. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, doi: 10.3334/CDIAC/OTG.LDEO_CORR**.**

INTRODUCTION

The LDEO underway pCO_2 measurements are made by monitoring CO_2 concentrations in carrier gas equilibrated with seawater in a shower-type equilibrator. Seawater is pumped continuously into and through a gas-water equilibrator, and its temperature is measured using a temperature sensor immersed in the equilibration chamber. The temperature and salinity of seawater is monitored with a thermosalinograph (TSG) unit located near the water intake near the ship's bow for the in situ values, and the water is delivered via a pump-pipe system to the pCO_2 equilibrator, which is generally located in the mid-ship or aft section of ship some distance from the intake. Since the temperature of sample water is changed due to pump actions and heat conduction through the pipe, the pCO_2 value measured in the equilibrator are corrected to the TSG temperature, which represents the in situ temperature. However, in order to obtain the temperature change, the time lag for the transit of water to the equilibrator must be taken into consideration. In our previous data reports, we assumed that the time lag was negligibly small and computed the temperature change using the TSG and equilibrator temperatures recorded at the same time. In this report, we present a statistical method developed for estimating the temperature corrections with time lag, and show several cases representing different conditions. The corrections are applied to all the individual pCO_2 values obtained using the LDEO underway pCO_2 systems operated aboard RVIB *Palmer*, RV *Gould* and USCGC *Healy*, which sail mostly in the polar oceans. The revised values are reported in Version 2014, LDEO Global Ocean Surface Water Partial Pressure of CO_2 Database, ORNL/CDIAC-160, NDP-088 (V2014).

METHOD

During the transit of a parcel of water from the TSG to the pCO_2 equilibrator through a pipe, water temperature is altered due to heat exchange with the surroundings. The difference between the equilibrator and TSG temperatures varies from ship to ship and many other factors including the pumping system construction, pumping rate, water temperature, ship's speed and others, and must be measured in order to correct the pCO_2 value measured at the equilibrator temperature to the corresponding TSG temperature. In some cases, the transit time was determined by correlating marker events (such as sharp temperature steps in water column). For example, temperature, salinity, pCO_2 and other properties were determined for waters pumped continuously through a few hundred meters long tubing towed behind RVIB *Palmer* (Hales and Takahashi, 2002). The temperature-salinity data were recorded at the water intake and at the shipboard laboratory once a second, and the transit time for sample water was determined from the difference in the arrival times with a precision of a few seconds in about 10 minutes of transit time during a Ross Sea expedition (Hales and Takahashi, 2004).

On the other hand, in our routine underway pCO_2 program, surface ocean water is pumped in from an intake (commonly located near the ship's bow at several meters below the sea surface) to the pCO_2 system located near the mid-ship or the stern, and the water temperatures at the intake and in the pCO_2 equilibrator are measured. The air-water equilibrator is a flow-through shower-type unit, which had a volume of about 15 liters (5 liters of gas space and 10 liters of water) with an e-folding response time of 30 to 45 seconds depending on the water flow rate (normally ~10 liters/minute). The large equilibrator volume was necessitated for providing greater operational stability and preventing flooding during continuous operations for 24 hours a day throughout a year whenever ships are at sea. The equilibrated carrier gas was dried and then pumped through the infrared CO_2 analyzer for three minutes until the readings became stable, and stopped for 20 seconds in order to minimize the effect of pressure fluctuations on CO_2 concentration readings. The pCO_2 value is recorded once every 3 minutes while the gas flow was stopped, and the temperature and salinity data were also recorded at the same time. Because of this recording frequency, the transit time of water could not be routinely determined based upon the direct correlation of marker signals. With this limitation of the data acquisition frequency, we have developed a simple statistical method for synchronizing TSG temperatures with equilibrator temperatures. Examples for the procedures used for estimating time lag corrections for temperature are presented below for the LDEO underway pCO_2 systems being operated aboard RVIB *Palmer*, RV *Gould* and USCGC *Healy*. The individual pCO_2 values measured at equilibrator temperatures are corrected to the corresponding TSG temperatures after the time lag corrections are made.

DATA ANALYSIS

1) RVIB N. B. Palmer Data

1-a) N. B. Palmer Cruise 14/6:

Analysis of the data from Palmer Cruise No. 6 in 2014 (14/6) in the South Atlantic is discussed below as an example. The (Equilibrator temperature – TSG temperature) differences are plotted as a function of TSG temperature (Figure 1). Shown are the temperatures recorded in 3-minute intervals starting on day 181.1 and ending on day 223.1 in 2014. During this period, Palmer started north from Punta Arenas, Chile, in the sub-Antarctic water (~4 °C), sailed in the warm (~22 °C) South Atlantic (Mid-Atlantic Ridge area, 21.0°S, 14.2 °W) for 10 days and returned to the Falkland area (48.2 °S, 54.6 °W) in the cold water regime (~6 °C). The top panel shows the temperature differences when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment). The middle panel shows the values when the TSG time was advanced by one step of recorded time (~3 minutes) to correct for the transit time of pumped water from the TSG to the pCO_2 equilibrator; and the bottom panel shows the values when the TSG time was advanced by 2 steps (~ 6 minutes). It is evident that the standard deviation around the linear regression line (± 0.018 °C with 3-minute time lag corrections) is improved significantly in the middle panel in comparison with the top and bottom panels (±0.051 °C with no time lag and ±0.049 °C with 6 minutes time lag, respectively). The standard deviation after the time lag corrections were made is consistent with the precision of temperature measurements of ±0.01 °C. We, therefore, advanced the TSG data by one-step (~3 minutes) for time lag adjustments, and corrected each individual pCO_2 value to the corresponding TSG temperature. We consider that further refinements of the time lag is not warranted because the pCO_2 values were recorded at 3 minutes time intervals and the pumping rate varies with time during the cruise.

Note that the mean differences between the equilibrator and TSG temperatures are not affected by the time lag adjustments, and remain unchanged at 0.0928 °C throughout the temperatures ranging from 4°C to 23°C. This suggests that the warming of the pumped water was nearly constant within ±0.02 °C throughout the cruise in this temperature range. However, as seen the middle panel for one step time adjustment, slight decrease in the warming is noticed as SST increased as indicated by the linear regression: (TEQ-TSG) = -0.0020 x TSG + 0.1316.

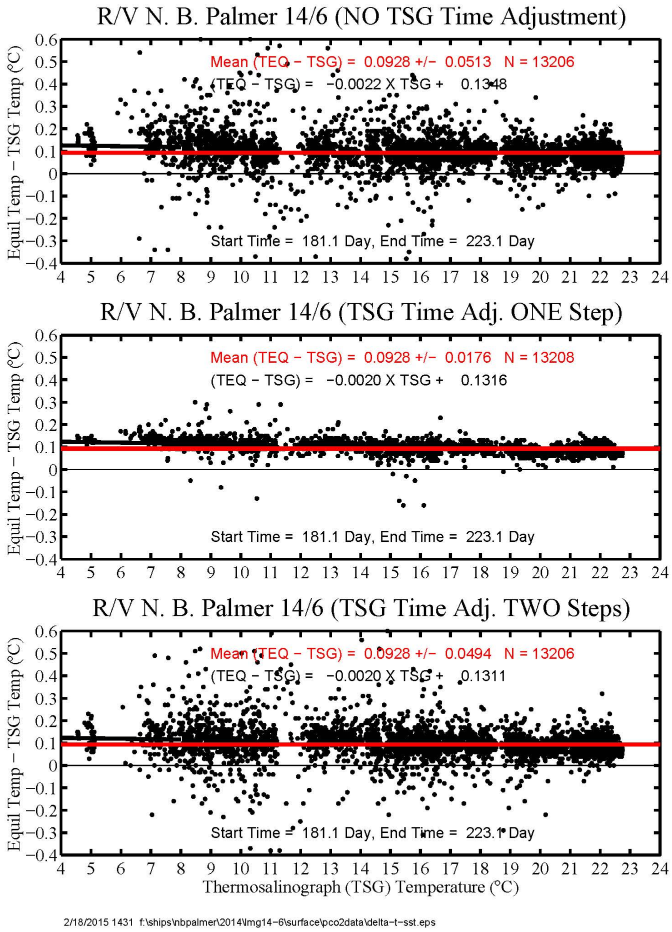

Figure 1 – The (Equilibrator – TSG) temperature difference plotted as a function of TSG temperature observed during Palmer Cruise 6 in 2014 (14/6) in the South Atlantic. The top panel shows the data when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment); the middle panel the values when the TSG time was advanced by one step of record intervals (~3 minutes) to correct for the transit time of pumped water from the TSG to the pCO_2 equilibrator; and the bottom panel the values when the TSG time was advanced by 2 steps (~ 6 minutes). A significant improvement in the standard deviation around the linear regression line (± 0.018 °C for 3-minute time lag corrections) is observed in the middle panel in comparison with the top and bottom panels (±0.051 °C for no time lag and ±0.0494 °C for 6 minutes time lag, respectively).

As seen in the top panel (no time adjustment), the temperature differences scatter as much as ± 0.4 °C from the mean, and the scatter is reduced to about ± 0.1 °C as the result of time lag corrections. The corresponding scatter of pCO_2 values are as large as ± 6 uatm (= 0.4 °C x 16 uatm $°C^{-1}$). After the temperature corrections are made, the scatter of pCO_2 values caused by the mismatch of the equilibration and TSG temperatures is reduced to the level of ± 1.5 uatm (= 0.1 °C x 16 uatm $°C^{-1}$). The temperature effect on pCO_2 of 16 uatm $°C^{-1}$ is based on the ($\partial \ln pCO_2 / \partial T$) of 0.0423 $°C^{-1}$ (Takahashi et al., 1993) and a mean pCO_2 of 375 uatm. The pCO_2 data thus corrected are listed in the revised database.

1-b) *Palmer* Data Corrections for 1994-2014:

While most of the *Palmer* data are corrected satisfactorily with a time lag of 3 minutes, some need a 6-minute lag as illustrated with the Gould 12/12 data (see Section 2-b). The results of analysis and the mean time lag used for correcting the cruise data undertaken 1994 through 2014 are listed in Table 1. Of 118 legs, the data from 113 legs were corrected by 1 step (~3minutes), and 5 legs were corrected by 2 steps. A total of 1,390,836 pCO_2 data are corrected and are listed in Version 2014.

Table 1 – Summary of the time lag analysis for the 1994-2014 Palmer pCO_2 data. Mean SST suggests general areas where the ship was operated. The time adjustment of **One Step** corresponds to about 3 minutes and **Two Steps** to about 6 minutes of lag time.

	Cruise ID	Data	Mean	Adjusted			Cruise ID	Data	Mean	Adjusted
Year	YY/NN	Count	SST(°C)	Steps		Year	YY/NN	Count	SST(°C)	Steps
1994	94/06	7,844	0.08	1		2002	02/01	25,114	1.83	1
	94/08	456	14.53	1			02/02	25,321	-0.33	1
	94/11	750	13.27	1			02/04	29,699	-1.41	1
1995	95/02	6,963	1.81	1			02/05	8,419	22.82	1
1996	96/03	12,181	2.88	1			02/06	6,769	16.47	1
	96/04	4,985	2.94	1			02/07	5,536	26.51	1
	96/05	2,527	4.15	1			02/09	6,930	1.01	1
	96/06	7,524	0.72	1		2003	03/01	8,062	-1.13	1
1997	97/01	7,290	-0.02	1			03/02	13,928	-1.78	1
	97/02	824	11.87	1			03/04	9,838	22.85	1
	97/03	973	9.83	1			03/05	7,426	0.22	1
	97/07	4,889	9.45	1			03/1A	6,017	-1.65	1
	97/08	14,109	-0.72	1			03/4A	17,138	1.07	1
	97/09	12,305	-0.85	1			03/5A	4,482	0.75	1
1998	98/01	19,706	-0.87	1		2004	04/01	12,296	-0.44	1
	98/02	22,474	3.97	1			04/02	17,701	-1.34	1
	98/04	11,908	5.13	1			04/03	9,456	10.95	1
	98/05	13,156	22.17	1			04/04	22,754	4.79	1
	98/06	10,818	23.90	1			04/06	14,276	13.04	1
	98/07	4,888	4.89	1			04/08	21,952	0.90	1
1999	99/02	10,907	-0.83	1			04/09	14,443	0.75	1
	99/03	5,888	0.44	1		2005	05/01	5,736	0.73	1
	99/04	11,705	0.11	1			05/02	8,263	-0.27	1
	99/09	27,412	-0.65	1			05/05	3,982	4.72	1
2000	00/01	27,483	-1.32	1			05/06	19,033	-1.49	2
	00/02	12,777	0.84	1			05/07	9,501	7.60	2
	00/03	8,457	-1.48	1			05/08	18,381	-0.09	2
	00/04	5,985	0.35	1			05/1B	7,494	13.12	2
	00/05	3,956	1.04	1		2006	06/01	16,174	1.27	2
	00/06	7,552	18.97	1			06/02	7,740	3.86	1
	00/08	19,474	0.17	1			06/03	10,005	-0.25	1
	00/7A	7,655	-0.27	1			06/06	17,563	-0.49	1
2001	01/01	23,241	-0.22	1			06/08	17,257	0.17	1
	01/02	7,841	8.65	1			06/2A	14,468	0.06	1
	01/03	19,558	-0.86	1			06/7A	9,242	7.37	1
	01/04	21,482	-1.54	1						
	01/05	29,637	-1.77	1						
	01/06	9,760	-0.80	1						
	01/07	23,657	0.13	1						

Table 1 (continued) – Summary of the time lag analysis for the 1994-2014 *Palmer* pCO_2 data. Mean SST indicates general areas where the ship was operated. The time adjustment of **One Step** corresponds to about 3 minutes and **Two Steps** to about 6 minutes of lag time. A total of 1,390,836 data have been corrected.

Year	Cruise ID YY/NN	Data Count	Mean SST(°C)	Adjusted Steps
2007	07/01	14,963	-0.06	1
	07/02	20,768	-0.98	1
	07/03	12,792	0.19	1
	07/09	14,749	-1.26	1
	07/10	8,548	3.72	1
	07/11	6,059	8.00	1
2008	08/01	6,875	2.30	1
	08/02	8,563	-1.40	1
	08/03	8,330	0.05	1
	08/04	9,300	9.02	1
	08/05	13,525	2.32	1
	08/06	10,861	0.30	1
	08/08	9,195	-0.61	1
2009	09/01	19,302	0.32	1
	09/02	15,159	0.74	1
	09/05	984	10.90	1
	09/08	10,830	2.65	1
2010	10/01	20,712	0.24	1
	10/02	16,371	0.15	1
	10/03	13,402	-0.31	1
2011	11/01	10,568	-0.06	1
	11/02	23,640	-0.86	1
	11/03	12,435	2.91	1
	11/04	2,364	1.51	1
	11/05	15,603	-0.53	1
	11/07	8,155	4.11	1
2012	12/03	13,582	-1.47	1
	12/07	3,877	-1.37	1
	12/08	1,637	5.48	1
	12/10	10,545	0.69	1
2013	13/02	16,261	-0.52	1
	13/03	9,426	6.55	1
	13/04	4,123	0.07	1
	13/05	8,980	17.84	1
	13/09	8,809	-1.09	1
	13/0A	3,130	4.81	1
	13/10	19,737	-0.19	1
2014	14/02	14,498	0.39	1
	14/03	14,700	11.86	1
	14/06	13,217	19.50	1
	14/07	8,919	-1.10	1
	14/08	7,664	0.23	1
	14/09	6,990	-1.44	1
	14/10	7,295	-0.05	1

2) RV *L. M. Gould* Data

2-a) RV *L. M. Gould* Cruise 14/4:

Analysis of the data obtained during the *Gould* Cruise No. 4 in 2014 (14/4) across the Drake Passage, Antarctica, is presented here as an example. The (Equilibrator temperature – TSG temperature) differences are plotted as a function of TSG temperature observed. Figure 2 shows the temperatures recorded at 3-minute intervals during the cruise started at Punta Arenas on day 98.5 in 2014, sailed across the Drake Passage, worked in the Palmer LTER area, and returned to Punta Arenas on day 138.9. The top panel shows the data when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment); the middle panel the values when the TSG time was advanced by one step (~3 minutes) to account for the transit time from the TSG to the pCO_2 equilibrator; and the bottom panel the values when the TSG time was advanced by 2 steps (~ 6 minutes). Significant improvement in the standard deviation around the linear regression line (± 0.0547 °C for 3-minute time lag corrections) is observed in the middle panel in comparison with the top and bottom panels (±0.070 °C for no time lag and ±0.065 °C for 6 minutes time lag, respectively). We, therefore, accept one-step (~3 minutes) time lag corrections for this cruise. The standard deviation for the corrected temperatures is greater but nearly consistent with the precision of the measured temperatures of ± 0.2 °C.

Figure 2 shows that the temperature difference is about 0.4 °C on the average for waters colder than 0°C, whereas it is reduced to about 0.25°C for warmer waters of 7 °C to 8 °C as indicated by the regression line (the heavy black line in all three panels). This is in contrast to the Palmer data (Figure 1), that exhibited nearly constant temperature off-set between the equilibrator and TSG. This may be accounted for by that cold waters pumped through the pipe in ship's warm interior were warmed more than the warmer waters due to the increase temperature differences between the sample water and the ship's interior temperatures. For this reason, the temperature off-set is also affected by the pumping rate of seawaters. After the 3-minute time lag correction was made (the mid-panel), the scatter of (Teq – TSG) values varies as much as ± 0.15 °C in waters colder than about 0°C, whereas, for the warmer waters, it is about ± 0.05 °C, which is consistent with the precision of measurements. The larger variation in cold waters may be attributed partially to the presence of eddies and steep meridional SST gradients, as well as to the variability in ship's operational conditions including underway pumping rates of sample waters.

As the result of the temperature corrections, the individual pCO_2 values are corrected up to ± 5 uatm (= 0.3 °C x 16 uatm °C^{-1}). However, the mean of pCO_2 corrections for each cruise is found to be less than ± 1 uatm (= 0.05 °C x 16 uatm °C^{-1}).

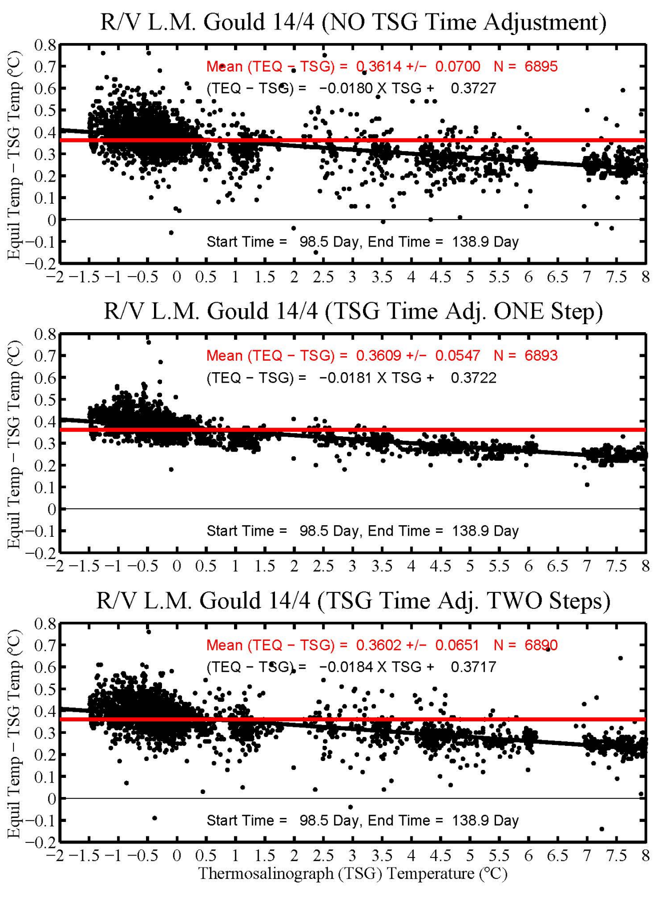

Figure 2 – The (Equilibrator temperature – TSG temperature) difference plotted as a function of TSG temperature observed during the Gould 14/4 cruise across the Drake Passage, Antarctica. The top panel shows the data when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment); the middle panel the values when the TSG time was advanced by one step (~3 minutes) to account for the transit time from the TSG to the pCO_2 equilibrator; and the bottom panel the values when the TSG time was advanced by 2 steps (~ 6 minutes). A significant improvement in the standard deviation around the linear regression line (± 0.055 °C) is observed in the middle panel in comparison with the top and bottom panel (±0.070 °C for no time lag and ±0.065 °C for 6 minutes time lag, respectively).

2-b) RV *L. M. Gould* Cruise 12/12:

Analysis of the data obtained during the *Gould* Cruise 12 in 2012 (12/12) across the Drake Passage, Antarctica, is presented as an example for the cases which required greater time corrections than 3 minutes. The (Equilibrator – TSG) temperature differences are plotted as a function of TSG temperature. Figure 3 shows the temperatures recorded in 3-minute intervals during the cruise started at Punta Arenas on day 310.0 in 2012, sailed across the Drake Passage, worked in the Palmer LTER area (64.1°S, 61.8 °W), and returned to Punta Arenas on day 328.3. The top panel shows the data when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment); the middle panel the values when the TSG time was advanced by one step (~3 minutes) to account for the transit time from the TSG to the pCO_2 equilibrator; and the bottom panel the values when the TSG time was advanced by 2 steps (~ 6 minutes). The uncorrected temperature data (top panel) scatter as much as ± 0.4 °C above and below the regression line. Significant improvement in the standard deviation around the linear regression line (± 0.113 for 6-minute time lag corrections) is observed in the bottom panel in comparison with the top and middle panels (±0.135 for no time lag and ±0.122 for 3 minutes time lag, respectively). The variance of the corrected data is consistent with the precision of measurements. We, therefore, accept two-step (~6 minutes) time lag corrections for the Gould Cruise 12 in 2012 (12/12). Figure 3(the heavy black line) also shows that the temperature difference is on the average about 0.7 °C in waters colder than 0°C, whereas it is reduced to about 0.45°C in 7 °C waters. The off-set, which represents the amount of warming through the pumping system, is nearly twice as large as that observed for Cruise 14/4 due likely to slower pumping rates.

Our assessment of the 6-minute lag time is consistent with the analysis made by David Munro and Colm Sweeney of University of Colorado (personal communication, 2014), who sent us an unpublished report entitled "Log Correction of LGM pCO_2 data: Data from LGM 1212" (in the PowerPoint format, dated March 12, 2014). Using the 30-second interval TSG data and 3-minute interval equilibrator temperature data, they computed the correlation coefficients for the TSG and equilibrator temperature data recorded over 2.5 days in a temperature range of -1.5 °C to 8 °C, and found the maximum correlation for a time lag of 6.1 (+1.3 or -3.7) minutes. Their results are consistent with our analysis.

As the result of the temperature corrections, the individual pCO_2 values are corrected up to ± 6 uatm (= 0.4 °C x 16 uatm °C^{-1}). However, the mean of pCO_2 corrections for each cruise is found to be less than ± 0.2 uatm (= 0.01 °C x 16 uatm °C^{-1}).

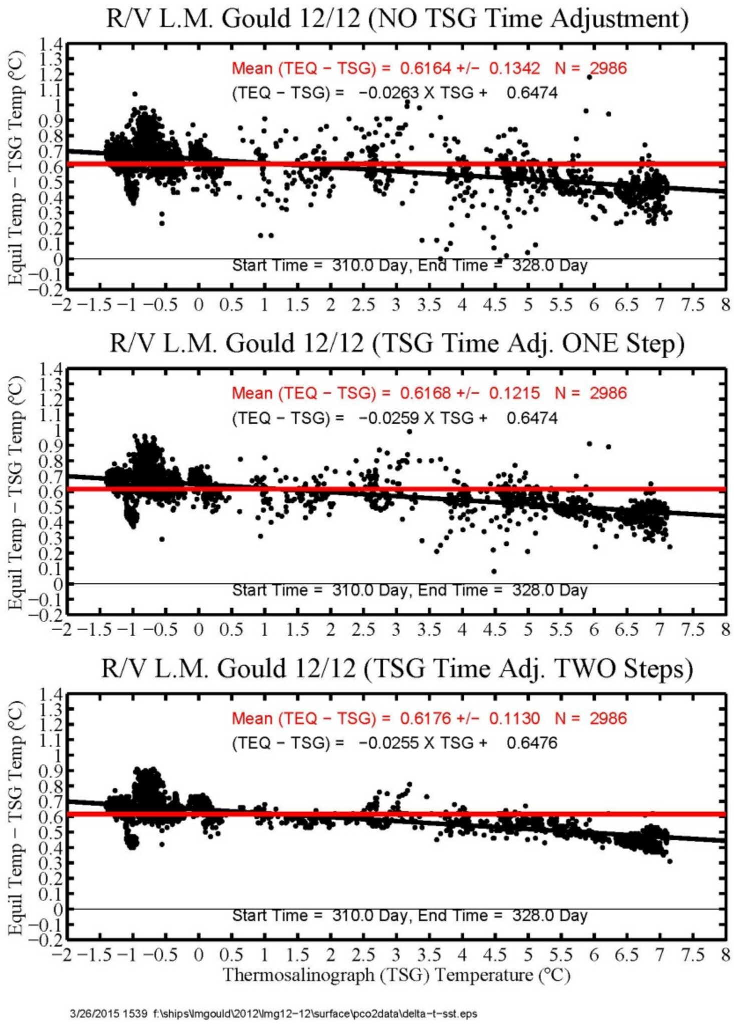

Figure 3 – The (Equilibrator temperature – TSG temperature) difference plotted as a function of TSG temperature observed during the Gould 12/12 cruise across the Drake Passage, Antarctica. The top panel shows the data when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment). The middle panel shows the values when the TSG time was advanced by one step (~3 minutes) to account for the transit time from the TSG to the pCO_2 equilibrator; and the bottom panel the values when the TSG time was advanced by 2 steps (~ 6 minutes). A significant improvement is evident in the bottom panel for 6 minutes time lag correction.

2-c) RV *L. M. Gould* Data, 2002-2015:

The *Gould* data obtained all the cruises starting the 2002 (02/1B) through 2015 (15/01) are analyzed for time lag correction, and the results are summarized in Table 2. Of 140 Gould cruises, the data for 113 of them are corrected for 3-minute time lag (one step adjustment) and those for 27 are corrected for 6 minutes (2 steps). A total of 742,984 pCO_2 values thus corrected are listed in our LDEO ocean surface water database, Version 2014.

Table 2 – Summary of the time lag analysis for the 2002-2015 RV *Gould* pCO_2 data. Mean SST indicates general areas where the ship was operated. The time adjustment of **One Step** corresponds to about 3 minutes and **Two Steps** to about 6 minutes of lag time.

Year	Cruise ID YY/NN	Data Count	Mean SST (°C)	Adjusted Steps
2002	02/1B	2,731	4.15	1
	2/2	1,879	3.1	1
	2/3	8,659	-0.95	1
	02/4A&B	4,815	2.26	1
	2/5	6,787	-1.4	1
	2/6	2,332	2.28	1
	2/7	2,937	1.84	1
	2/8	3,137	1.09	1
	2/9	8,196	0.84	1
2003	3/1	13,831	1.89	1
	3/2	4,118	1.22	1
	3/3	5,721	1.86	1
	3/4	9,302	0.85	1
	03/4A	4,629	1.79	1
	03/5A	5,774	-0.69	1
	3/5	2,683	2.42	1
	3/6	2,495	1.34	1
	3/7	3,450	0.64	1
	3/8	3,758	1.79	1
	3/9	12,288	-0.27	1
2004	4/1	12,556	1.94	1
	4/2	14,222	2.36	1
	4/3	2,100	2.89	1
	4/4	5,510	-0.01	1
	4/5	3,797	1.46	1
	4/6	2,609	2.21	1
	4/7	2,835	2.34	1
	4/8	3,849	20.11	1
	4/10	4,539	19.08	1
	4/11	3,165	1.55	1
	4/12	2,091	0.73	1
	04/13A	4,014	1.68	1
	4/14	10,916	1.67	1

Year	Cruise ID YY/NN	Data Count	Mean SST (°C)	Adjusted Steps
2005	5/1	14,087	1.21	1
	5/2	11,409	0.98	1
	5/3	2,337	4.26	1
	5/4	1,377	2.12	1
	5/5	3,664	1.61	1
	5/6	3,126	2.36	1
	5/7	2,837	2.03	1
	5/8	4,440	23.15	1
	5/9	3,876	21.72	1
	5/11	2,436	1.73	1
	5/12	3,032	1.74	1
	5/14	3,899	2.05	1
	05/14A	6,485	0.53	1
2006	6/1	10,537	1.63	1
	6/2	8,137	3.68	1
	6/3	3,072	5.03	1
	06/3A	2,987	5.76	1
	6/4	2,601	3.61	1
	6/5	11,145	1.13	1
	6/6	3,480	1.32	1
	6/8	2,932	1.48	1
	6/10	1,560	0.82	1
	6/11	3,457	0.55	1
	6/12	5,211	0.91	1
	6/13	2,172	3.04	1
	6/14	2,230	3.62	1
2007	7/1	12,376	3.68	1
	7/2	3,766	3.49	1
	7/3	2,439	4.31	1
	7/4	2,637	3.41	1
	7/5	6,996	0.55	1
	7/6	5,290	0.44	1
	7/7	2,246	0.79	1
	7/12	3,200	0.86	1
	7/13	2,753	1.14	1
	7/15	3,395	0.97	1
	7/17	9,960	0.42	1

Table 2- (continued) Summary of the time lag analysis for the 2002-2015 RV *Gould* pCO_2 data. Mean SST indicates general areas where the ship was operated. The time adjustment of **One Step** corresponds to about 3 minutes and **Two Steps** to about 6 minutes of lag time.

Year	Cruise ID YY/NN	Data Count	Mean SST (°C)	Adjusted Steps	Year	Cruise ID YY/NN	Data Count	Mean SST (°C)	Adjusted Steps
2008	8/1	12,083	1.61	1	2012	12/1	12,526	0.91	2
	8/2	9,211	2.02	1		12/2	5,165	2.67	2
	8/3	2,377	4.1	1		12/3	3,598	3.02	2
	8/4	4,178	2.11	1		12/4	3,497	2.08	2
	8/6	6,374	0.5	1		12/5	4,216	1.43	2
	8/7	4,254	0.81	1		12/6	2,688	0.39	2
	8/8	3,972	0.76	1		12/9	1,710	17.27	2
	8/9	6,172	-0.1	1		12/10	2,945	0.99	2
	8/10	8,197	-0.29	1		12/11	1,581	0.65	2
	8/11	2,259	1.43	1		12/12	2,986	1.18	2
	8/12	3,587	1.1	1		12/13	1,608	1.39	1
2009	9/1	11,692	1.61	1		12/13A	3,616	2.04	2
	9/2	10,836	2.18	1	2013	13/1	11,052	1.62	1
	9/3	5,577	3.47	1		13/2	2,056	3.09	1
	d 09/5	15,326	0.15	1		13/3	4,222	3.26	1
	09/6A	3,300	1.02	1		13/4	5,591	1.76	1
	9/7	2,048	21.24	1		13/5	3,187	2.22	1
	9/9	5,278	0.37	2		13/6	4,130	0.82	1
	9/10	3,885	0.19	2		13/9	3,377	0.96	1
	9/11	9,030	-0.13	1		13/10	2,310	1.38	1
2010	10/1	10,939	0.7	1		13/11	3,772	0.41	1
	10/2	10,895	1.87	1		13/12	7,273	0.3	1
	10/3	3,996	2.32	1	2014	14/1	11,808	1.2	1
	10/4	8,592	0.26	1		14/2	5,848	1.29	1
	10/6	3,619	0.42	2		14/3	1,561	3.82	1
	10/7	3,002	1.21	2		14/4	6,829	0.55	1
	10/8	1,107	2.89	2		14/6	8,326	-0.63	1
	10/10	8,275	1.21	2		14/8	2,040	1.21	1
2011	11/1	10,947	1.7	2		14/9	1,709	0.79	1
	11/2	6,854	0.72	2		14/10	6,884	-0.13	1
	11/3	2,383	4.16	2		14/11	6,514	0.94	1
	11/4	3,584	2.33	2	2015	15/1	7,476	1.59	1
	11/5	8,866	0.94	2					
	11/6A	2,965	1.49	2					
	11/8	2,840	0.75	2					
	11/9	3,301	0.72	2					
	11/10	6,161	0.18	2					
	11/11	3,612	2.51	2					

3) USCGC *Healy* Data, 2011-2015

USCGC *Healy*, whose home port is Seattle, WA, operates in the Gulf of Alaska, the Bering Sea and the Arctic Ocean. Scientific activities are undertaken mostly during the summer months, and the pCO_2 measurements have been made during the months of June through September in each year. Our pCO_2 program was started in May, 2011.

The time-lag corrections applied for the Healy data are summarized in Table 3. We observe that the time-lag for the Healy data vary from 2 steps (~ 6 minutes) to 4 steps (~ 12 minutes), which are considerably larger than those experienced aboard the RVIB Palmer and RV Gould. The longer time-lag may be attributed to the longer pipe line needed for the larger ship and to slower pumping rates. An example for the Healy data is shown in Section 3-a.

Table 3 – Summary of the time lag analysis for the USCGC *Healy*, 2011- 2015 pCO_2 data. Mean SST indicates general areas where the ship was operated. The time adjustment of **Two Steps** corresponds to about 3 minutes, **Three Steps** to about 9 minutes, and **Four Steps** to about 12 minutes of lag time. The total number of the data corrected is 160,332.

Year	Cruise ID YY/NN	Data Count	Mean SST (°C)	Adjusted Steps
2011	11/5	17,399	0.50	4
	11/4	11,234	1.79	3
	11/3	18,195	0.39	3
	11/2	18,915	5.00	4
	11/1	3640	17.75	2
2012	12/3	8,690	2.48	3
	12/2	20,409	0.03	4
	12/1	1,968	11.12	3
2013	13/2	11,138	9.00	3
	13/1	14,867	1.34	3
2014	14/3	9,354	7.35	3
	14/2	10,878	2.00	4
	14/1	11,723	1.33	4
2015	15/1	1,922	4.33	4

3-a) USCGC *Healy* Cruise 15/1:

Figure 4 shows the temperature data obtained in the Bering Sea and the coastal Beaufort Sea during the 7 day period (Day 195.5 through day 201.5) in mid-July, 2015. Some temperature data show that the temperature data collected in the sub-zero seawater temperatures present some puzzling features such as that the equilibrator temperatures are colder than the TSG temperatures by as much as 0.8 °C. This may be attributed to strong lateral and/or vertical temperature gradients formed in the melting ice field. It is also possible that the temperature sensor in TSG was crusted with ice.

The top panel shows the data when the Equilibrator temperature and the TSG temperature readings were taken at the same recorded time (i. e. No Time Adjustment); the middle panel the values when the TSG time was advanced by 4 steps (~12 minutes) to account for the transit time from the TSG to the pCO_2 equilibrator; and the bottom panel the values when the TSG time was advanced by 5 steps (~15 minutes). When no time lag corrections are made (top panel), the temperature differences are as large as ± 1 °C. Significant improvement in the standard deviation around the linear regression line (± 0.146 °C for a time lag correction by four steps) is observed in the middle panel in comparison with the top and bottom panels (± 0.403 °C for no time lag correction and ±0.151 °C for five step time lag correction, respectively). We, therefore, accept a four-step (~12 minutes) time lag correction for this cruise. The maximum scatter of the (Equilibrator – TSG) temperatures is reduced from about ± 1 °C down to about ± 0.2 °C after the data are corrected for a time lag of 12 minute.

As the result of the temperature corrections, the individual pCO_2 values, which were reported in the previous LDEO database, are corrected by up to ± 16 uatm (= 1 °C x 16 uatm $°C^{-1}$). However, after corrections are made, the mean of pCO_2 corrections for each cruise is found to be about ± 2.5 uatm (= 0.15 °C x 16 uatm $°C^{-1}$).

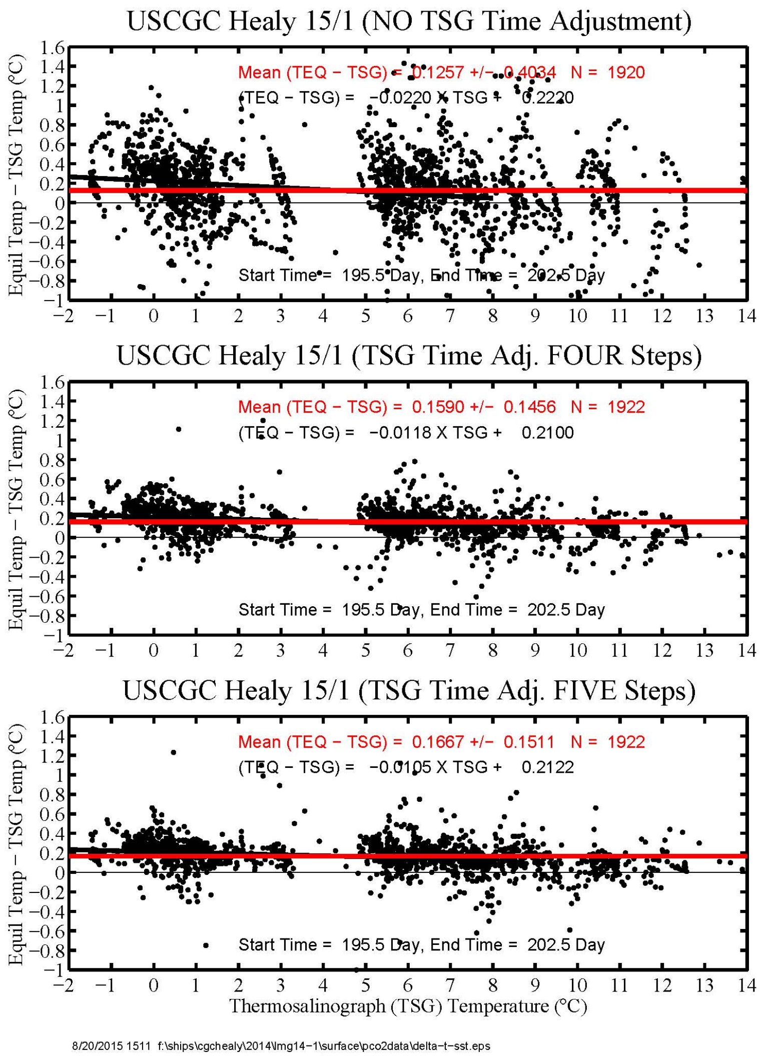

Figure 4 - The (Equilibrator temperature – TSG temperature) differences plotted as a function of TSG temperature observed during the USCGC Healy 15/1 cruise in the Gulf of Alaska and the Arctic Ocean. The top panel shows the data when both temperature readings were taken at the same recorded time (i. e. No Time Adjustment); the middle panel the values when the TSG time was advanced by FOUR steps of recorded time (~12 minutes) to correct for the time lag of pumped water; and the bottom panel the values when the TSG time was advanced by FIVE steps (~15 minutes). Standard deviation for the middle panel is smallest (0.146 °C) compared to the No adjustment (0.403 °C) and the FIVE step adjustment (0.151°C) cases.

CONCLUSION

Aboard research ships, pCO_2 in ocean water is investigated using the LDEO underway pCO_2 systems, which consists of an air-water equilibrator and IR CO_2 analyzer. The pCO_2 values measured at equilibrator temperatures are recorded at every 3 minutes along with the temperatures of equilibration and in-situ seawater. We developed a simple method for estimating the time lag between the equilibrator and in-situ temperatures caused by the transit of pumped seawater from the bow of ship to the pCO_2 system. The variance of the (Equilibrator temperature – TSG) temperature differences was minimized by advancing the equilibrator temperatures by one 3-minute time step at time. About 2.3 million pCO_2 data reported from the ships RVIB *Palmer*, RV *Gould* and USCGC *Healy* have been corrected for the time lag using the method. The time lag is estimated to be about 3 to 6 minutes for the Palmer and the Gould, and up to 15 minutes for the Healy. The time lag introduced errors in the uncorrected (equilibration – in-situ) temperatures of up to ± 0.5 °C for the Palmer and Gould, and up to ± 1 °C for the Healy. We find that the standard deviation of the (equilibration-in-situ) temperature differences for the corrected data set is about ± 0.1 °C, which consistent with the precision of temperature measurements. Accordingly, the seawater pCO_2 values, which were originally reported by assuming no time lag, are corrected by up to ± 8 uatm for the Palmer and Gould data and up to ± 16 uatm for the Healy data using the ($\partial \ln pCO_2 / \partial T$) of 0.0423 $°C^{-1}$ (Takahashi et al., 1993) is used. As the result of the corrections, the random errors in pCO_2 caused by the temperature-induced errors are reduced to within ± 1 uatm. The mean of uncorrected pCO_2 values for each cruise is found to be virtually unchanged from that of the corrected values.

REFERENCES CITED

Hales, B. and Takahashi, T. (2004). High-resolution biogeochemical investigation of the Ross Sea, Antarctica, during the AESOPS (U. S. JGOFS) Program. Global Biogeochem. Cycles, 18, No. 3, GB3006, doi. 10.1029/2003GB002165.

Hales., B. and Takahashi, T. (2002) . The pimping SeaSoar: A high-resolution seawater sampling platform. Jour. Oceanic and Atmospheric Technology, 19, 1096-1104.

LDEO Global Ocean Surface Water Partial Pressure of CO_2 Database, ORNL/CDIAC-160, NDP-088 (V2014)

Munro, D. and Sweeney, C. (personal communication) "Log Correction of LGM pCO_2 data: Data from LGM 1212" (in the PowerPoint format, dated March 12, 2014).

Takahashi, T., Olafsson, J., Goddard, J., Chipman, D. W. and Sutherland, S. C., (1993). Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. Global Biogeochemical Cycles, 7, 843-878.